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Ultrafast Nonlinear Spectroscopy with Chirped Optical Pulses

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Ultrafast four-wave mixing experiments using chirped-pulse excitation of a dye molecule in solution are reported and analyzed. Novel time-delayed signals are observed which are assigned to coherent Stokes-Raman scattering involving the excited state. Numerical calculations of four-wave mixing with linearly chirped pulses based on a stochastic dynamical model show that the signal near zero delay time is extremely sensitive to the presence or absence of slow fluctuations in the solute-solvent interaction.

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Optical dynamics at ultrafast time scales is generally best studied by nonlinear optical experiments with ultrashort light pulses. The rapid development of techniques to generate almost transform-limited pulses of less than 10 fs [1] has greatly stimulated this line of research. In these experiments the excitation of a system occurs much faster than the relevant relaxation times. This is the so-called impulsive limit of the system-field interaction.

In this Letter ultrafast transient-grating experiments with chirped laser pulses on resorufin in dimethylsulfoxide will be reported. It will be shown that this new approach to the study of dephasing dynamics is especially powerful in elucidating the nature of the fluctuations that affect the optical transition. We also report on a novel coherent Raman signal, which is generated at a delay time when the instantaneous frequency difference between the excitation beams matches a vibrational frequency.

In a linearly chirped pulse a large bandwidth is combined with phase control during a long non-transform-limited pulse. In such a light wave, time and frequency are connected in a well-defined way: The front end of the pulse contains the lowest-frequency components, while the tail end of the pulse comprises the highest frequencies. During the pulse a continuous shift of frequency occurs (the "chirp") from low to high. The potential of using chirped pulses in the study of optical dynamics was first realized by Yajima and co-workers [2,3], who analyzed two-beam scattering experiments using the Bloch equations. It was predicted [2] that impulsive and chirped excitation yield the same coherent transients. This idea was supported by four-wave mixing experiments on doped semiconductor glasses [3]. We will show, however, that chirped and impulsive excitation give the same transients only for strongly inhomogeneously broadened systems.

Chirped pulses with a large bandwidth were generated by injecting amplified colliding-pulse mode-locked laser pulses into an optical fiber to increase the spectral bandwidth by self-phase modulation and the pulse duration by linear dispersion [4]. The resulting spectral width of the pulses leaving the fiber was about 2600 cm^{-1} while the duration was about 1 ps, as measured in an autocorrelation experiment. The chirp that is generated in this way is close to being linear:

$$E_i(t) = e_i(t) \exp\{-i[(\omega_i^0 + \tfrac{1}{2} b_i t)t - \mathbf{k}_i \cdot \mathbf{r}]\} . \quad (1)$$

Here $e_i(t)$ is the pulse envelope, $\omega_i(t) = \omega_i^0 + b_i t$ is the instantaneous frequency, ω_i^0 is some offset frequency, and b_i is the chirp rate. The optical frequency can thus be swept through material resonances in a controlled way; the phases of the frequency components are locked.

The layout of the experiment is shown in Fig. 1. Two pulses with wave vectors $\mathbf{k}_1$ and $\mathbf{k}_2$ are directed to a sample; the signal is observed as a function of the relative delay τ between the pulses in the direction $\mathbf{k}_s = 2\mathbf{k}_2 - \mathbf{k}_1$.

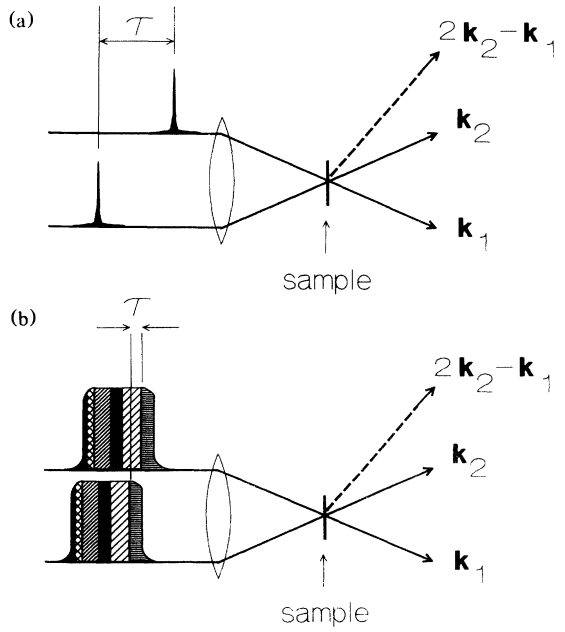

FIG. 1. Layout of nonlinear scattering experiments. The signal in the direction $2\mathbf{k}_2 - \mathbf{k}_1$ is observed as a function of the relative delay τ. The upper panel (a) depicts impulsive scattering and the lower one (b) chirped scattering.

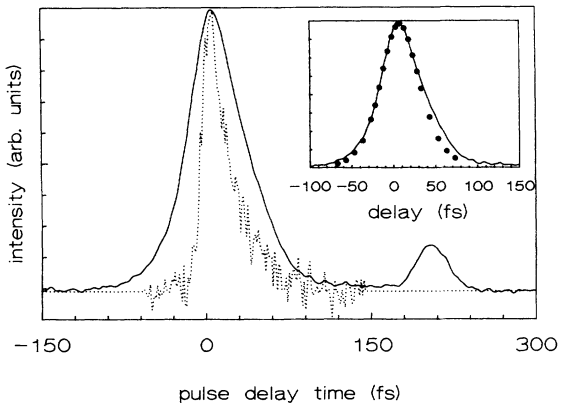

FIG. 2. Two-pulse delayed scattering signal for resorufin in dimethylsulfoxide. The solid trace was obtained with chirped pulses of 1-ps duration; the dotted trace with compressed pulses with a duration of about 9 fs. Inset: Numerical calculations (solid dots) of the chirped signal (solid line).

The average power of the signal is detected by a photomultiplier and processed by a lock-in amplifier. The sample consisted of a flowing jet stream of dimethylsulfoxide with a thickness of 60 μm containing resorufin of a concentration of 1 mM.

The experimentally observed two-beam scattering signal for chirped-pulse excitation is displayed in Fig. 2. For comparison the impulsive photon-echo signal [5] is also included. This figure clearly shows that for chirped-pulse excitation the transient signal is distinctly broader than for impulsive excitation and that an additional transient is observed at a delay of about 200 fs.

With impulsive excitation many vibrational levels will be excited. Vibrational wave packets are then launched on the ground- and excited-state potential-energy surfaces leading to multiple interferences in the scattered signal [6]. In contrast, by employing chirped pulses the optical transitions of multilevel systems are excited sequentially and all system transitions participate in the signal without interference.

The delay time τ can be directly associated with an instantaneous frequency difference between the two pulses. For small delays this means that both pulses simultaneously interact with the same system transition. For large delays the instantaneous frequency difference becomes of the order of the vibrational energies of the system. Both pulses with their fixed frequency difference are then swept through two different optical resonances at the same time. When $\pm(\omega_2-\omega_1)_{\text{inst}}=\omega_{\text{vib}}$ the scattering in the direction $\mathbf{k}_s=2\mathbf{k}_2-\mathbf{k}_1$ actually consists of the coherent (anti-)Stokes-Raman frequencies $\omega_s=2\omega_2-\omega_1$.

In the case of resorufin only two optical transitions contribute significantly to the observed nonlinear signals [5]: the 0-0 transition and a vibronic transition at 545 cm^{-1} from the origin. This leads to a (weak) beat in the impulsive decay of Fig. 2. In the chirped experiment the signals from both transitions just add up for small delays. When the delay is so large that the instantaneous frequency difference between the two pulses matches a vibrational energy, a Raman resonance shows up. This occurs at 200 fs. For positive delays, pulse 2 trails pulse 1 and hence $\omega_2<\omega_1$, which means that the observed signals around 200 fs can be classified as coherent Stokes-Raman scattering (CSRS). Obviously for negative delays ($\omega_2>\omega_1$) the corresponding anti-Stokes signals (CARS) are missing. A possible explanation for this asymmetry is that in a fully resonant four-level system (including a ground-state vibration of about the same frequency) excited-state CARS experiences less resonance enhancement than excited-state CSRS.

By changing the amount of chirp in the pulses the Raman resonance occurs at a different delay. The chirp rate can easily be adjusted by the introduction of dispersive elements in the beam path. Figure 3 shows how the vibrational resonance is attained for larger relative delays when the chirp is made slower. By knowing the chirp rate these dynamic scattering experiments can thus be used to identify vibrational frequencies.

The actual shape of the Raman resonance at 200-fs delay is determined by both vibrational and electronic dephasing parameters. A detailed discussion of these effects will be presented elsewhere [7]. In this Letter we will concentrate on the signals at small delays, when both pulses act simultaneously on the same system transition. The properties of the transients are then determined by electronic dephasing processes alone.

For a quantitative description of the signals near zero pulse delay, it is necessary to consider the general theory for four-wave mixing. Using standard time-domain perturbation theory [8], the third-order polarization with wave vector $2\mathbf{k}_2-\mathbf{k}_1$ for a two-level system is

$$
\begin{aligned}
&P^{(3)}(\omega_{ba},\mathbf{r},t,\tau)\\
&\propto(-i)^3|\mu_{ab}|^4 e^{i(2\mathbf{k}_2-\mathbf{k}_1)\cdot\mathbf{r}}\\
&\times\int_0^\infty dt_3\int_0^\infty dt_2\int_0^\infty dt_1\{R_1(t_3,t_2,t_1)e^{-i\omega_{ba}(t_3-t_1)}E_2(t-\tau-t_3)E_2(t-\tau-t_3-t_2)E_1^*(t-t_3-t_2-t_1)\\
&\qquad+R_2(t_3,t_2,t_1)e^{-i\omega_{ba}(t_3+t_1)}E_2(t-\tau-t_3)E_1^*(t-t_3-t_2)E_2(t-\tau-t_3-t_2-t_1)\}\,. \qquad (2)
\end{aligned}
$$

Here τ is the pulse delay time, μ_{ab} is the dipolar transition moment of the two-level system, $R_{1,2}$ are nonlinear response functions, ω_{ba} is the transition frequency, and $E_{1,2}$ are the applied fields.

The response functions R_1 and R_2 depend on the nature of the coupling between the system and bath. When the

correlation time of the interaction between the system and bath is very short compared to the system dynamics itself, the influence of the bath on the system can be described by time-independent parameters (the Markov approximation). In those circumstances the Bloch equations hold and the relaxation functions are equal:

$$R_{1,2}(t_3,t_2,t_1)=e^{-\Gamma_{ab}(t_3+t_1)}(e^{-\gamma_a t_2}+e^{-\gamma_b t_2}). \quad (3)$$

Here γ_i is the population decay rate out of level i, and $\Gamma_{ab}=\frac{1}{2}(\gamma_a+\gamma_b)+\hat{\Gamma}_{ab}$ is the inverse dephasing time $(T_2)^{-1}$. In a more general stochastic model [9,10], in which the correlation time of the interaction between the system and bath can be of arbitrary time scale, the relaxation functions are considerably more complex and differ from each other [10]:

$$R_1(t_3,t_2,t_1)=\Phi^+(t_3,t_2,t_1)(e^{-\gamma_a t_2}+e^{-\gamma_b t_2}), \quad (4a)$$

$$R_2(t_3,t_2,t_1)=\Phi^-(t_3,t_2,t_1)(e^{-\gamma_a t_2}+e^{-\gamma_b t_2}), \quad (4b)$$

where

$$\Phi^{\pm}(t_3,t_2,t_1)=\exp\{-(\Delta^2/\Lambda^2)[e^{-\Lambda t_3}+e^{-\Lambda t_1}+\Lambda(t_3+t_1)-2\pm e^{-\Lambda t_2}(e^{-\Lambda t_3}+e^{-\Lambda t_1}-e^{-\Lambda(t_3+t_1)}-1)]\}. \quad (5)$$

Here the parameters Δ and Λ are the amplitude and the inverse correlation time of the stochastic fluctuations, respectively. The difference between R_1 and R_2 arises from the fact that during the propagation of the system during the times t_1, t_2, and t_3, a coherent superposition state is inverted (R_1) or not (R_2). When the correlation time is finite, this inversion allows for rephasing of coherences and thus different decay characteristics [5,10,11].

When very slow fluctuations are present in a system [12], in addition to the degrees of freedom that lead to the (non-)Markovian dynamics discussed above, rephasing processes are possible for the total polarization $P^{(3)}_{\text{inhom}}$, which is the polarization of Eq. (2) summed over a distribution of resonance frequencies $g(\omega_{ba})$:

$$P^{(3)}_{\text{inhom}}(\mathbf{r},t,\tau)=\int_{-\infty}^{\infty}d\omega_{ba}\,P^{(3)}(\omega_{ba},\mathbf{r},t,\tau)g(\omega_{ba}). \quad (6)$$

The shape of the observed transients of Figs. 2 and 3 depends on the relative contribution of the R_1 and R_2 terms to the nonlinear polarization of Eq. (2). In the impulsive limit (chirp rate $b\rightarrow\infty$) the R_1 part of Eq. (2) dominates due to the explicit time ordering of the fields (first the field E_1 has to be applied, then twice the field E_2). It was checked numerically that with a very fast chirp rate the same polarization is induced as with delta-pulse excitation. For slower chirp rates, the relative contributions from R_1 and R_2 depend strongly on the amount of inhomogeneity present. When the width of the distribution $g(\omega_{ba})$ is substantial, the contribution from the rephasible R_1 part will be much larger than the R_2 part, which lacks the rephasing capability. *Therefore, for optical transitions dominated by very slow fluctuations (large inhomogeneous broadening) the coherent transients induced by chirped-pulse or impulsive excitation are expected to be the same.* This situation was theoretically described and experimentally studied by Yajima and co-workers [2,3].

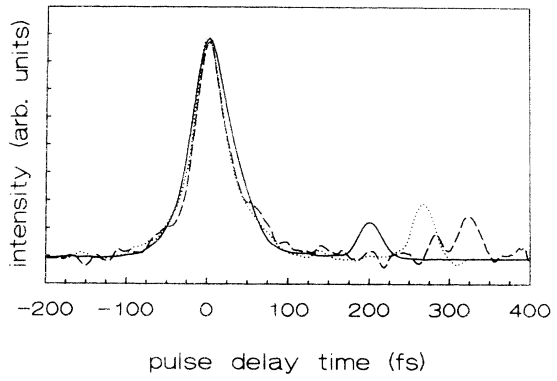

FIG. 3. Nonlinear scattered signal obtained with chirp rates of 2.6 cm^{-1}/fs (solid line), 2.1 cm^{-1}/fs (dotted), and 1.7 cm^{-1}/fs (dashed). The intensities were normalized at $\tau=0$.

When rephasing processes are less important, however, the situation is different. For impulsive scattering the R_2 part is then still negligible, due to the explicit time ordering of the fields, but it should be taken into account for chirped scattering. Since R_2 contributes mainly for negative delays, and R_1 almost exclusively for positive delays, the signal with chirped excitation will be much more symmetrical around $\tau=0$ than for impulsive excitation. Therefore, a qualitative comparison between impulsive and chirped measurements can readily provide important information on the presence or absence of inhomogeneous broadening in a system.

We have recently shown [5] that a stochastic model provides a consistent description of the optical dynamics of resorufin in dimethylsulfoxide. The nonlinear polarization which results from chirped-pulse excitation can thus be calculated by inserting Eqs. (1) and (4) in Eq. (2). The observed signal of Figs. 2 and 3 is the cycle-averaged intensity due to this nonlinear polarization:

$$I_{\text{signal}}(\mathbf{r},\tau)=\int_0^{\infty}dt\,|P^{(3)}(\omega_{ba},\mathbf{r},t,\tau)|^2. \quad (7)$$

Since the spectral distribution of the pulses was reasonably flat over the frequency range of interest, in the calculation of the signal we could take $e_{1,2}(t)=e^0_{1,2}$ and $\omega_1^0=\omega_2^0=\omega^0$ in Eq. (1) without any loss of generality. The exact value of the offset frequency is not very important. It may be the lowest frequency that the pulse carries, but any frequency away from the material resonances will do. The rise and fall of the pulse intensity well outside of the resonances is of no consequence. We took $\omega_0=2.9$ PHz, while the resonance frequency was $\omega_{ba}=3.16$ PHz. The chirp rate was taken to be $b=2.6$ cm^{-1}/fs. The stochastic parameters Δ and Λ of the re-

laxation functions Φ^+ and Φ^- in Eq. (4) were taken from Ref. [5]: $\Delta = 41$ THz and $\Lambda = 27$ THz. Population relaxation was neglected since the time scale of this process is much longer than that of the coherence decay.

The result of the numerical evaluation, based upon Monte Carlo integration [7] of the fourfold integrals of Eqs. (2) and (7), is shown in the inset of Fig. 2. In view of the fact that no adjustable parameters were involved, we consider the agreement between calculation and experiment to be satisfactory. For the parameter values of this experiment both the R_1 and the R_2 parts of the polarization contribute significantly to the signal. With considerable inhomogeneous broadening the R_2 term is negligible and the R_1 part alone yields a very asymmetric trace around zero delay. This is clearly not observed, so we conclude that no significant inhomogeneity is present in this system. The spectrum of resorufin in dimethylsulfoxide is apparently completely dominated by an ultrafast non-Markovian dynamical process.

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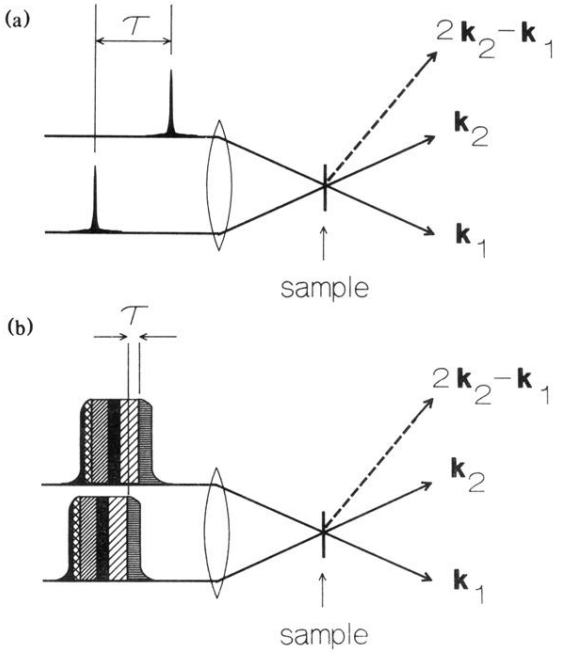

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